

特约专栏

# Photocatalytic Ceramic Foam Filter: Application Research Progress and Prospect

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**Abstract:** Photocatalytic ceramic foam filter, the composite of high photoactive  $\text{TiO}_2$  nano materials and three dimensional porous ceramic foam materials, has been widely applied in the field of air/water purification, owing to its characteristics of high photoactivity, large surface area, large flowing flux and ceramic heat/chemical resistance, recycling probability. Applications have been in the fields of industrial exhaust deodorization, agriculture pesticide degradation using sunlight, sterilization of laboratories and hospitals, high-speed train air purification, and so on. The application research progress, problem and future prospect of photocatalytic ceramic foam filter are summarized.

**Key words:** photocatalyst; ceramic foam filter; application; air/water purification

CLC number: TQ051.8<sup>+</sup>5; TQ174.75<sup>+</sup>8 Document code: A Article ID: 1674-3962(2010)08-0027-03

## 光催化泡沫陶瓷过滤器的应用研究现状和展望

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**摘要:** 高活性的光催化二氧化钛纳米材料与高气孔率的三维多孔泡沫陶瓷材料复合, 得到的光催化泡沫陶瓷过滤器, 具备高活性、大表面积、大通量、以及陶瓷的耐高温、耐化学腐蚀、循环适用性, 在大气/水净化领域率先得到了广泛应用。在工业领域的废气脱臭处理、在农业领域的农药废水太阳光降解、在医疗卫生领域的实验室医院空气杀菌处理、在交通领域的高速列车空气净化等, 已经展开应用。综述了国内外光催化泡沫陶瓷过滤器的应用研究现状、问题及其发展趋势。

**关键词:** 光催化; 泡沫陶瓷过滤器; 应用研究; 大气/水净化

### 1 Introduction

$\text{TiO}_2$  photocatalyst, due to its low price, high photoactivity and safety to human being and environment guaranteed by history, has been widely applied in the fields of air/water purification<sup>[1-5]</sup>. Among varieties of  $\text{TiO}_2$  photocatalytic materials, photocatalytic ceramic foam filter, a composite of  $\text{TiO}_2$  and ceramic foam by utilizing the high active performance of  $\text{TiO}_2$  and the high resistance and large surface area of ceramic foam, has been commercialized recently and is getting more importance for industrial applications.

### 2 Applications in industrial deodorization

Experimental animal raising facility usually exhausts 24 hours everyday, and the odor complaint from residents is the main common problem for similar facilities. The exhaust contains several  $10^{-6}$  degrees of ammonia, acetaldehyde, trimethylamine

and organic acid such as n-butyric acid, etc. The condition is proper for photocatalytic deodorization treatment because the odor contaminations are low level, while the exhaust is at room temperature. Experimental animal raising facility exhaust deodorization is one of the success industrial applications for photocatalytic ceramic foam filter. One of the authors (Zhou) experienced the engineering of deodorization of 6 000  $\text{m}^3/\text{h}$  experimental animal exhaust in Tokyo in 2005. The odor concentration was 130 before treatment and 32 after treatment, and deodorization effect reached about 75%.

Kitchen exhaust of shopping mall is usually deodorized by active carbon filter, and photocatalytic ceramic foam filter has already been applied in this field recently. Except oil substances, main odor contaminations of kitchen exhaust are several  $10^{-6}$  degrees of ammonia and acetaldehyde, etc. Kitchen exhaust is necessary to be deoilingly treated before deodorization treatment by photocatalytic ceramic foam filter. One of the examples of 4 000  $\text{m}^3/\text{h}$  shopping mall kitchen exhaust treatment in Tokyo in 2006 showed that the odor concentration was 3 200 before treatment, remained to be 3 200 after deoiling treatment, decreased to 790 after first pass photocatalytic deodorization and further decreased to 500 after second pass photocatalytic deodorization. This is another success example of photocatalytic ceramic foam filter for industrial use, and new-built shopping malls become to adopt photocatalytic deodorization system recently in Japan.

Rubbish odor of rubbish pressing and transiting facilities in

Received date: 2010-07-29

Foundation item: China-Japanese Cooperation Program (XDHT2008296A);  
Xiamen University, Introduction of Qualified Personnel  
Items(0044-x12101)

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urban areas of China is one of the main problems needing to be deodorized. Rubbish pressing and transiting facilities are usually built near or inside resident areas, rubbish odor and noise bother residents. A field experiment of deodorization using photocatalytic ceramic foam filter was conducted by an equipment under the conditions of 4 passes, 0.09 m<sup>2</sup>/pass, 300 m<sup>3</sup>/h air treatment capacity, and the result showed the probability of applying photocatalytic technology in rubbish deodorization. Figure 1 showed the odor sensor's values of the air at the indoor (before deodorization) and the outdoor (after deodorization) of the equipment. The odor value before deodorization was not constant and varied largely during rubbish pressing process. The peak value reached about 4 to 5 times higher than the valley value. After deodorization by photocatalytic method, the odor value maintained low value which was much lowered than that before deodorization. The chemical substance concentrations before and after deodorization listed in Table 1 showed that main odor substances were ammonia and methyl mercaptan, and those degradations reached 88.2% and 67.9% after photocatalytic deodorization, respectively. From Table 2, odor concentration degraded 95.4% averagely after deodorization, comparing with odor concentration before treatment.

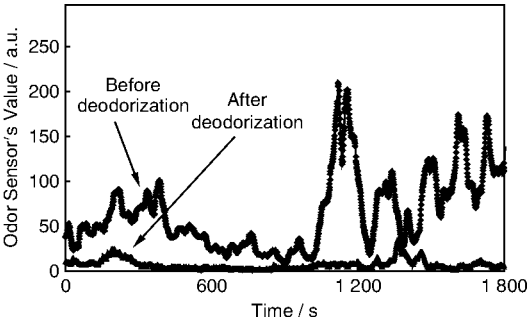


Fig. 1 Photocatalytic deodorization effect of the field test for rubbish pressing and transiting facility by using photocatalytic ceramic foam filters

Table 1 Chemical substance concentrations before and after deodorization of the field test

	Chemical substance concentration/10 <sup>-6</sup>		
	H <sub>2</sub> S	NH <sub>3</sub>	CH <sub>3</sub> SH
Indoor of testing equipment	0.001	17.3	0.002 8
Outdoor of testing equipment	ND	2.04	0.000 9
Degradation percent	—	88.2%	67.9%

Table 2 Odor concentrations before and after deodorization of the field test

		Odor concentration/a. u.		Average
		Sample 1	Sample 2	
Indoor of testing equipment	Sample 1	1 738		1 694
	Sample 2	1 650		
Outdoor of testing equipment	Sample 1	81		78
	Sample 2	75		
Deodorization percent	Sample 1	95.3%		95.4%
	Sample 2	95.5%		

Pretreatment plays important role and is necessary in some industrial deodorization applications of photocatalytic ceramic foam filter. Oil particles, dust particles and moisture are particularly considered to be pre-filtered out during deodorization engineering processes, otherwise deodorization effects are affected largely. The affect of moisture on photocatalytic activity of photocatalytic ceramic foam filter has been tested in 40%, 60% and 90% relative humidity at 40 °C by degradation of acetaldehyde as a probe by our group, the result shows that the CO<sub>2</sub> forming rate under UV illumination of 40% humidity is the largest, that of 60% humidity is almost the same, and that of 90% humidity is the lowest and is only about half of that of 40% humidity, i. e., photoactivity of photocatalytic ceramic foam filter is restrained when humidity reaches a high level such as 90%. The result also shows that the adsorption of reaction substance of acetaldehyde drops with the increase of humidity, giving that the reason of that high humidity hinders photoactivity of photocatalytic ceramic foam filter can be reasonably connected with the drop of physical adsorption.

3 Applications in agriculture

Photocatalytic ceramic foam filter has been field tested to degrade pesticide of agriculture liquid waste and TOC (total organic carbon) of agriculture nutrient solution, reported by research groups of Tokyo University and Kanagawa Agriculture Techno-Center in Japan<sup>[6]</sup>. Rice seeds have to be disinfected by using pesticides and rinsed several times before cultivation, resulting in agriculture liquid waste containing pesticides. Treatment area of 2.25 m<sup>2</sup> of photocatalytic ceramic foam filter was used under sunlight to degrade 40 L pesticide liquid waste. The concentrations of ipconazole pesticide and TOC decreased largely when the treatment started. After 4 days, ipconazole pesticide was non-detected, and the degradation effect was confirmed by fish toxicity test<sup>[6]</sup>. The recycling nutrient solution was treated by photocatalytic ceramic foam filter under sun-light in tomato nutrient solution cultivation. The recycling system was consisted by treatment area of 1.2 m<sup>2</sup> of photocatalytic ceramic foam filter, reserving tank of 40 L and supplying tank of 100 L, and the batch treatment method was used. Among testing period of 10 months, the nutrient solution with photocatalytic treatment was transparent and TOC was 7 ~ 28 mg/L, while that without photocatalytic treatment was brown and TOC reached 21 ~ 777 mg/L. Tomato harvests of nutrient solution with photocatalytic treatment increased by 40.8% in the 1<sup>st</sup> harvest and by 34.0% in the 2<sup>nd</sup> harvest during the testing period, comparing with that without photocatalytic treatment.

4 Applications in sterilization

Photocatalytic ceramic foam filter has been applied in sterilization of laboratories and hospitals, related fundamental and applications reported by research groups of Tokyo University and some companies in Japan<sup>[7-9]</sup>. The fundamental of sterilizing mechanism of Cu/TiO<sub>2</sub> film under very weak UV irradiation was reported to consist of two steps<sup>[7-8]</sup>. The first step is the partial decomposition of the outer membrane in bacteria cell envelope by a photocatalytic process, the second step is the permeation of the copper ions into the cytoplasmic membrane to sterilize bacteria, which explain why Cu/TiO<sub>2</sub> showing high sterilization effect even under weak UV illumination. High porosity (about 80% ~ 90%) of photocatalytic ceramic foam filter was used in the test of sterilization of 30 m<sup>3</sup> SUS laboratory<sup>[8]</sup>. Airborne microbe decreases by 30% ~ 40% even in the absence of UV illumination, but in this case, microbe is only captured by the filter and will

be released again with air flux. In the case of UV illumination, the survival rate of airborne microbe downs to 17% after 15 min, owing to that the microbe captured by the filter is sterilized by photocatalytic oxidization and can not be released again<sup>[8]</sup>. The practical applications of photocatalytic ceramic foam filter in laboratory raising rats and hospitals get satisfied effect of sterilization, and in the meantime, have also deodorization effect<sup>[8-9]</sup>.

## 5 Applications in high-speed train

The development of deodorization equipment using photocatalytic ceramic foam filter for high-speed train was conducted, as reported by JREA<sup>[10]</sup>. The target is to decompose the chemical substances of tobacco odor and to apply for tobacco rooms in high-speed train. A new coating technology was developed and the oxidizing decomposition ability improved largely, comparing to ordinary coating method<sup>[10]</sup>. The equipment has been applied in the new series of N700 high-speed train in Japan<sup>[10]</sup>. In China, the application technology of photocatalytic ceramic foam filter in high-speed train has been developed by related companies in collaboration with Xiamen University.

## 6 High photoactive materials

The research of high photoactive materials of photocatalytic ceramic foam filter is always a technical challenge. Noble metal deposited TiO<sub>2</sub> has been intensively studied, and the photoactivity improves owing to that the recombination of photo induced electrons and holes are restrained by noble metal deposition. In practical applications, Ag deposition is applied instead of noble metal. Ag/TiO<sub>2</sub> photocatalytic ceramic foam filter is developed, as reported by research groups in Japan<sup>[11-12]</sup>. Ag nano particles are homogeneously dispersed into TiO<sub>2</sub>, and the decomposition of H<sub>2</sub>S improves largely, comparing to that without Ag deposition<sup>[11]</sup>.

## 7 Conclusions

The industrial applications of photocatalytic ceramic foam filter have been widely extended recently, and the application research progress, problem and prospect are summarized mainly in the application fields of industrial deodorization, agriculture,

sterilization and high-speed train. Meanwhile, the importance of Ag/TiO<sub>2</sub> photocatalytic ceramic foam filter is emphasized.

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# 973 计划项目“水泥低能耗制备与高效应用的基础研究”进展顺利

我国水泥产量自 1985 年以来一直位居世界第一, 2009 年产量高达 16.4 万吨。水泥行业具有能耗高、污染重、二氧化碳排放多等特点, 尤其是生产过程中的烧、磨环节。如何降低水泥生产过程中的能量消耗, 减少二氧化碳排放, 对于节能减排具有重要意义。

973 计划项目“水泥低能耗制备与高效应用的基础研究”由南京工业大学沈晓东教授为首席科学家, 中国建筑材料研究院为依托单位。项目围绕水泥结构和熟料矿物组成、熟料分段烧成动力学及过程控制、水泥粉磨动力学及过程控制、水泥熟料和辅助性胶凝材料优化复合的化学和物理基础等重大科学问题开展研究, 在降低能耗研究方面取得了多项进展。项目从提高水泥熟料胶凝性能、降低水泥熟料烧成的热耗入手, 在研究熟料矿物质结构及形成机制基础上, 建立熟料微结构与性能关系, 研究熟料燃烧及快速冷却后能获得的阿利特高温稳态结构, 提出的改进熟料烧制方法生产每吨水泥可节约 12 kg 标准煤, 节煤效率约 10% 以上, 减少熟料使用量 20% 以上。同时, 项目在熟料分段烧成动力学及过程控制研究中, 通过不断尝试, 把燃烧温度从原来的 1 400 ℃降低为 1 300 ℃, 仅该环节就可降低烧成热耗 3% ~ 5%。此外, 项目还从燃烧学、水泥结构、水泥浆体组成等不同方面进行降低能耗的基础研究。(本刊通讯员)